Study of Bi-isonicotinic acid and Re(4,4'-dicarboxy-2,2'-bipyridine)$(CO)_3Cl$ on TiO_2 Surface

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Master of Science

by

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ABSTRACT

Dye-sensitized solar cells are promising for relatively high efficiency and low price compared to original thin-film model. The basic mechanism is that the dye molecules absorb light and are promoted into the excited electronic state. Thereafter the excited electron is transferred to TiO_2. However, there are not many models that allow us to understand the molecular processes that occurs in dye-sensitized solar cells. Our research goal is to figure out the configuration of dye molecule (bi-isonicotinic acid) adsorbed on a TiO_2 surface and to understand the molecular connection between the molecules and surface.

BIOGRAPHICAL SKETCH

Eun Kee Cho is a graduate student from Seoul, Korea.

She graduated with a Bachelor of Science in Chemistry in February 2018.

Coram deo

To my supportive family,

Sincere friends

and the love of my life, Shin Kim

ACKNOWLEDGMENTS

I would like to appreciate Professor Melissa A. Hines for giving me a great opportunity to participate in her project and for sincerely supporting the research.

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CHAPTER 1

Introduction and Background

1.1 Motivation

As we live as a generation of confronting environmental pollution and crisis in the traditional energy resources, the importance of alternative and sustainable energy has been more emphasized. Among the main renewable technologies such as hydropower, wind power, geothermal energy and bioenergy, solar energy has attracted significant industrial attention as it is abundantly available and increasingly efficient. Ever since the emergence of the photovoltaic cell, much research has been invested in the development of new solar cells with improved efficiency. Dye-sensitized solar cells (DSSCs) are one of the high-potential solar cell systems containing light-absorbing dye molecules on a semiconducting base[1]. Our research focuses on the development of a model system for investigations of the dye-surface interactions of the dye-surface interaction in DSSCs. Although the mechanism of the photogenerated electrons is well understood[2], detailed configuration of dye molecules is unclear. Several previous researches about how the dye molecules adsorb on the metal oxide surface have been performed mainly through computational simulations[3]. There are few studies that observed the atomic-level configuration of dye molecules on metal oxide surface. Therefore, this limited information between the dye molecules and the surface has become our strong motivation for the research. If we are able to get clean image of this surface with the dye molecules, we could incorporate the previous knowledge to understand the movement of electrons in the molecules more precisely. Understanding this molecular orientation can give insight into the photophysics of DSSCs and potential their improvement.

1.2 Background

1.2.1 Dye-sensitized solar cell

Dye-sensitized solar cells (DSSCs) are included in a thin-film solar cell forming a second-generation solar cell that has one or more thin layers of photovoltaic material deposited on a substrate. While the photovoltaic conversion efficiency is lower than the maximum level found in thin-film cells, DSSCs are still attracting much attention due to their relatively low cost and constantly improving performances.

DSSCs consist of three main layers: a transparent anode (fluoride-doped tin dioxide, F-TCO or TCO) which is deposited on the back of a glass plate, a conductive plate formed from TiO_2 nanoparticles with high surface area that is also highly porous and an iodide electrolyte spread on a conductive sheet[4]. These sheets are then bound together to prevent the liquid electrolyte from leaking. After TiO_2 is chemically bound to the glass via sintering, the plate is immersed in a photosensitive dye with a solvent. This leaves dye molecules on the surface of the TiO_2 via persistent covalent bonds.

Most of the high-efficiency DSSCs use ruthenium-based dye-molecules bound to TiO_2 nanoparticles which form part of the photoanode. The dye-molecule found in DSSCs plays a crucial role in the photon-converting mechanism. The overall process involved in DSSCs energy conversion consists of a following steps:

1. The incident photon is absorbed by the Ru dye molecule complex photosensitizers adsorbed on the TiO_2 surface
2. The photosensitizers are excited from the ground state(S) to the excited state(S*)
3. Excited electrons are injected into the conduction band of the TiO_2 electrode leading to the oxidation of the photosensitizer(S^+)

   $S+h\nu \rightarrow S^*$

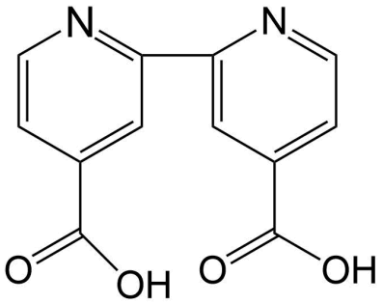
   $S^* \rightarrow S^+ + e^-$ (TiO_2)

4. The electrons injected in the TiO_2 conduction band are transported toward the back contact (TCO) and ultimately reach the counter-electrode through the circuit
5. The oxidized photosensitizer(S^+) accepts electrons from the I^- ion redox complex leading to regeneration of the ground state(S) as two I^- ions are oxidized to elementary iodine (which complexes with I^- to form the tri-iodide anion, I_3^-)

   $S^+ + e^- \rightarrow S$
6. The oxidized redox mediator, I_3^-, diffuses toward the counter electrode and is then reduced back to I^- ions.

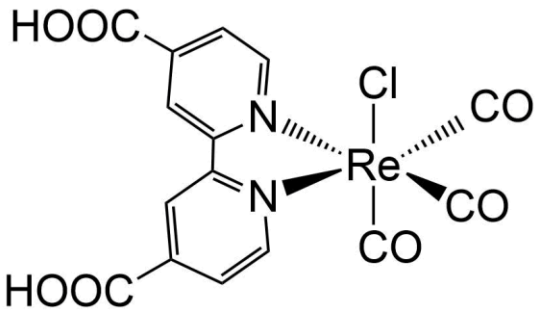
   $I_3^- + 2e^- \rightarrow 3I^-$

1.2.2 Bi-isonicotinic acid (4,4,'-dicarboxy-2,2'-bipyridine)



Bi-isonicotinic acid (4,4,'-dicarboxy-2,2'-bipyridine) is a ligand of organometallic dyes, frequently used in photoelectrochemical applications. Especially in DSSCs, it efficiently binds dye molecules with the surface of TiO_2 substrate. Since electron transfer kinetics largely related to the bonding of the anchor ligand to the substrate, bonding of the bi-isonicotinic acid to the semiconductor substrate plays an important role in improving performance of DSSCs[5]. It has been studied that the carboxyl group of the molecule is a key of bonding to the metal oxide surface[6].

1.2.3 Re(4,4,'-dicarboxy-2,2'-bipyridine)$(CO)_3Cl$



Re(4,4,'-dicarboxy-2,2'-bipyridine)$(CO)_3Cl$ is metal complex with modified bipyridine ligands. It is known as a photocatalyst in carbon dioxide reduction. Other complexes with modified bipyridine ligands have also been studied for electrocatalytic reduction of carbon dioxide[7]. Re complexes are covalently attached to the TiO_2 surface, increasing reductive ability. It is reported that Re complex binds through the carboxylate groups and exposes Re to the substrate[8].

1.2.4 X-ray Photoelectron Spectroscopy

X-ray Photoelectron Spectroscopy (XPS) is a quantitative spectroscopy that has high surface-sensitivity. XPS is useful to figure out the elemental composition and electronic state of the elements within a sample. Therefore, XPS is a critical technique to investigate and understand the adsorption of molecules to the surface[9].

When an incident X-ray beam hits the sample, electrons are emitted at an energy that is given by the difference between the energy of the incident X-ray photon and the binding energy of the ejected electron.

$$E_{kinetic,\ electrons} = E_{X\text{-}ray} - E_{binding,\ electrons}$$

As a result, the energy of the emitted electron is a sensitive indicator of the chemical identity and oxidation state of the emitting atom. Since electrons that penetrate the sample travel through materials and lose energy, some of the ejected electrons have lower energy than would be expected by the above equation.

CHAPTER 2

Research Objectives

2.1 Rationale for the Study

Ever since DSSC has been developed, many trials aiming to improve the efficiency have explored modification of each component which constitutes the DSSC. Researchers discovered the most efficient group of sensitizers in TiO_2-based DSSCs, bipyridyl complexes of ruthenium (II)[10], which has a strong and broad absorption band in the visible range due to metal to ligand charge transfer. Carboxylic or phosphonic acids are the preferred anchoring groups for dyes, because they can form esters on the oxide surface with good linkage stability. These anchoring groups are essential to efficiently couple electronic levels in the donor dye molecule to the relevant and acceptor levels of the semiconductor. However, much less is known about the chemical interactions between the dye molecule and the underlying substrate. For example, does the dye bond through one binding moiety (e.g., carboxylic acid group) or two? In this case of carboxylate-bound dyes, is the conjugation between the dye and the linking group maintained or does steric hinderance distort the binding? Do neighboring molecules interact, potentially leading to unwanted effects? Thus, most effort of this study was to fill this specific gap between the importance of dye molecules and their actual orientation on the surface.

2.2 Experimental Goal

This study was performed with two main goals in mind. Firstly, prior work has provided very little information about the dye molecule, leaving unknown even such fundamental information as whether the molecule is able to form a monolayer on the oxide surface. For this study, we used solution deposition techniques and identified

molecules using XPS. Obtaining the elemental information through XPS can demonstrate if molecules have successfully formed monolayers and provide a promising guideline for taking atomic-level images.

The second goal was to study molecular orientation with STM (Scanning Tunneling Microscopy), which gives atomic level information regarding the bonding between the adsorbed molecule and the oxide surface. In this preliminary study, although we were unsuccessful in obtaining a clean image from the STM on the first trial, the data from XPS reveals that the molecules have nearly formed a monolayer on the TiO_2, encouraging further trials for STM. Thus, our second goal corresponds to the future research plan in this study.

CHAPTER 3

EXPERIMENTAL METHODOLOGY

3.1 Finding Solution for bi-isonicotinic acid

3.1.1 Experimental Design

Our initial goal was finding a good solvent which can completely dissolve bi-isonicotinic acid. This is a critical starting point for all subsequent research because only in a solvent with high solute solubility and no tendency to form aggregates can we expect to successfully assemble a monolayer on the metal oxide surface. Undissolved solutes in the solution will produce crystallites on the metal oxide surface which will disturb monolayer assembly. Therefore, as a preliminary step, we have made a series of solutions using eight different solvents and observed whether it has precipitate in solution or not. We approached the solvent candidates in order of polar, polar aprotic and nonpolar solvent and in this experiment. Here we report polar solvents and polar aprotic solvents.

3.1.2 Experimental Procedure

Every solution was made with the same concentration; 0.5mM of the target solute, bi-isonicotinic acid, was added to different solvents. We dissolved the solute through sonication and heating (around boiling temperature of the solvents) with stirring.

3.1.3 Data Analysis

The following table shows the results of screening proper solvents. Against our expectations, we were unable to find a solvent system that both dissolved bi-isonicotinic acid completely and produced atomically clean monolayers. DMSO, DMF and Iso-propanol were able to dissolve the solute, but all three of them did not satisfy our

standards. We have eliminated DMSO from the final list due to its propensity for surface contamination. Since we aimed to make a sample with a monolayer of bi-isonicotinic acid on TiO_2, the solvent that dissolves the molecule should not remain on the sample. If the solvent tends to remain, it can disturb molecules from forming a monolayer. Moreover, the solvent molecules can be detected through XPS, making it difficult to analyze data accurately. DMF dissolved the solute at high temperature (90-100℃), but upon subsequent cooling back to room temperature, significant precipitation occurred. Iso-propanol was too poor a solvent to form solutions as concentrated as 0.5mM, though upon dilution by a factor of 10 (0.05mM in solute), a stable solution was formed. However, this concentration might be too diluted compared to other solutions to have accurate results.

Solvent	Bi-isonicotinic acid
Ethanol	Not dissolved
Methanol	Not dissolved
Acetonitrile	Not dissolved
DMSO	**Dissolved**
DMF	**Dissolved**
THF	Not dissolved
Iso-propanol	**Dissolved**
Toluene	Not dissolved

Table 1. Results in the Solvent

Finding a proper solvent for bi-isonicotinic acid was not as simple as we assumed before the experiment. This unexpected result forced us to change the original scope of our research plans and to investigate a different model system.

3.2 Re(4,4,'-dicarboxy-2,2'-bipyridine)(CO)$_3$Cl

3.2.1 Experimental Design

Since finding a proper solvent for bi-isonicotinic acid was not straightforward, we decided to solve the problem with Re compounds, which have bi-isonicotinic acid as a ligand. Several electronic state dynamics studies of Re(dcbpy)(CO)$_3$Cl (4,4'-dicarboxy-2,2'-bipyridine=dcbpy) on TiO_2 for photoreduction can be a clue for our initial goal. Hence, we started from synthesizing Re(dcbpy)(CO)$_3$Cl and made a sample with Re(dcbpy)(CO)$_3$Cl on the surface of TiO_2. Since Re(dcbpy)(CO)$_3$Cl includes bi-isonicotinic acid, also using carboxylic acid to form a bond with TiO_2, successfully making a monolayer with Re complex on TiO_2 will provide a higher possibility to succeed in the same experiment with bi-isonicotinic acid.

3.2.2 Experiment Procedure

Synthesizing Re(dcbpy)(CO)$_3$Cl

This compound was prepared with slight modifications, and with the following method from literature by Jonathan M. Smieja *et al*[7]. Procedure of the synthesis is in figure 1.

1. Re(CO)$_5$Cl (0.200g, 0.55 mmol) and 4,4'-dicarboxy-2,2'-bipyridine (0.130g, 0.55 mmol) was dissolved in 50mL of hot toluene and 20mL of methanol.
2. The reaction mixture was stirred under reflux for 1-hour with initial color change from clear to orange.

3. The reaction mixture was removed from heat after the 1-hour reflux, and the unreacted starting material was precipitated from solution in the freezer overnight.
4. After filtering out the white starting material, the bright orange filtrate was rotary evaporated to dryness.

Figure 1. Reacting $Re(CO)_5Cl$ and 4,4'-dicarboxy-2,2'-bipyridine under 1-hour reflux

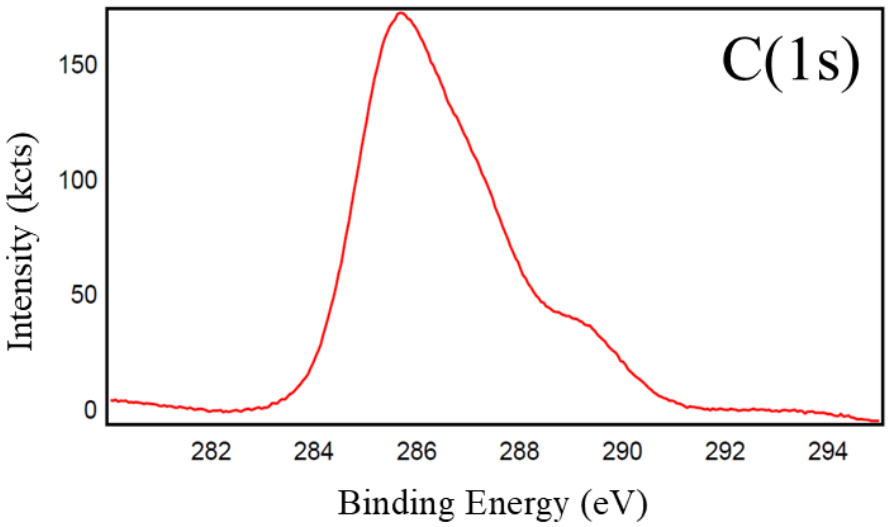
Preparing TiO_2(110) Crystal Sample

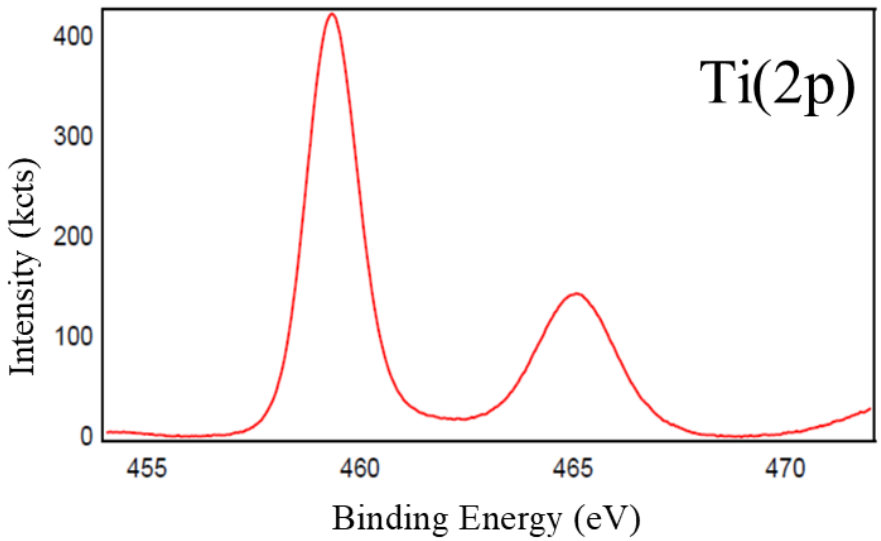
TiO_2 crystal sample was made through simply immersing TiO_2 in the solution for 20 minutes. Solution was made with 0.5 mM in the target solute, $Re(dcbpy)(CO)_3Cl$ with ethanol as a solvent.

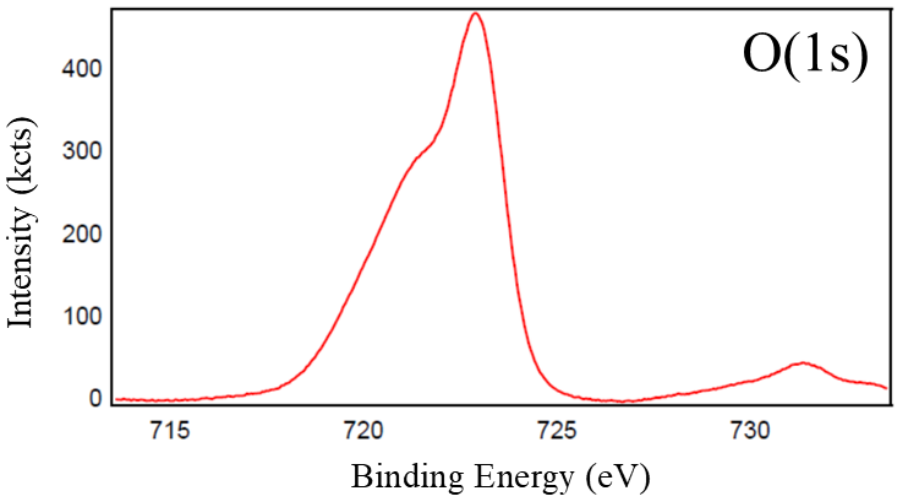
1. Rinse off the crystal with water for several times.
2. Put the crystal into a test tube filled with 2:1:1 ratio of water, hydrogen peroxide and ammonium hydroxide under heating (80°C) for 20 minutes. This process gives an atomically clean and atomically flat TiO_2(110) surface which is suitable for monolayer formation.
3. After cleaning process, dip the crystal into the solution (0.5mM) for 20 minutes at room temperature.

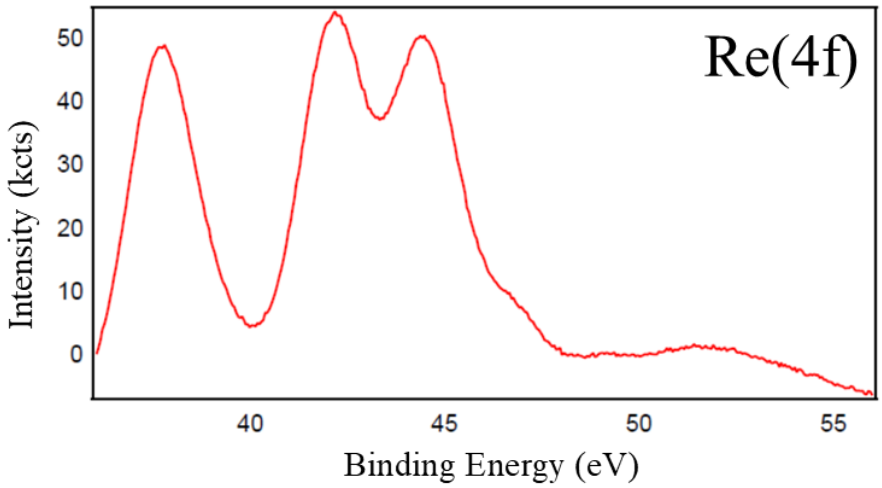
XPS

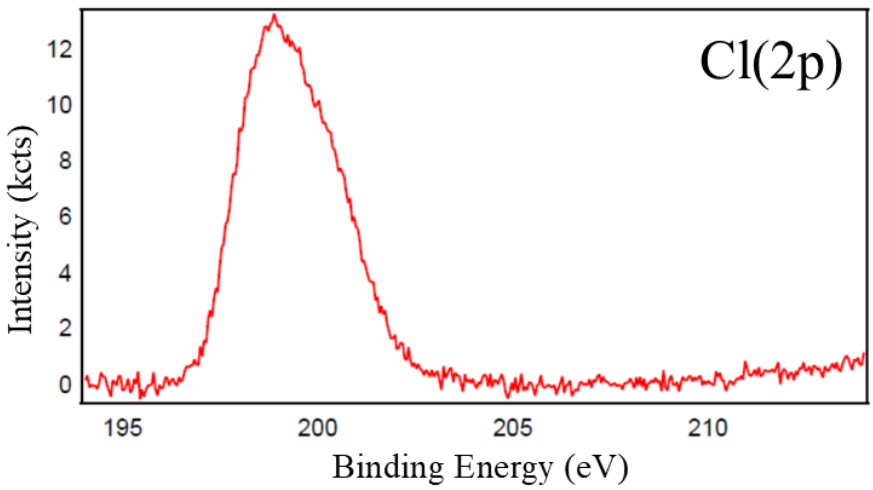
The identification of the monolayer on the surface was confirmed through XPS analysis (Figure 3). XPS was performed with non-monochromatic Mg K_α X-rays and the photoelectrons were collected at 70° from the surface normal. Tougaard baseline was removed from all reported spectra. Binding energy reference is based on National Institute of Standards and Technology (NIST) of the U.S. Department of Commerce.






O(1s)
Intensity (kcts)
400
300
200
100
0
715
720
725
730
Binding Energy (eV)


Re(4f)
Intensity (kcts)
50
40
30
20
10
0
40
45
50
55
Binding Energy (eV)


Cl(2p)
Intensity (kcts)
12
10
8
6
4
2
0
195
200
205
210
Binding Energy (eV)

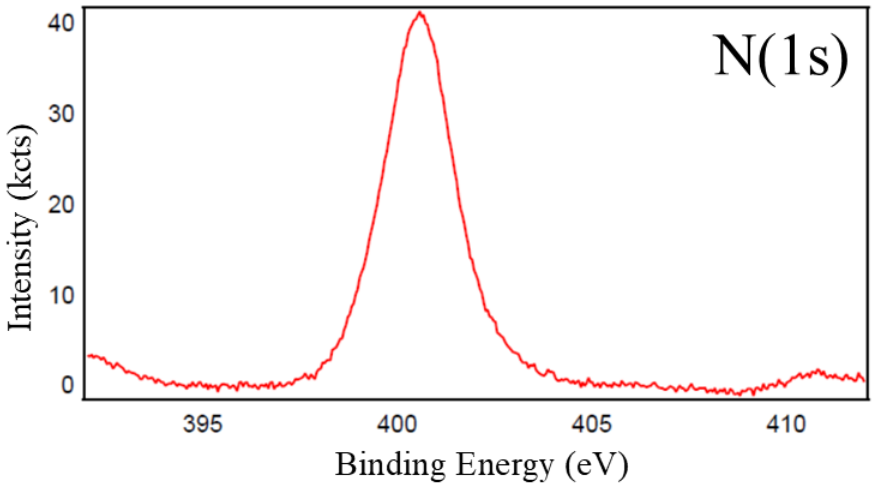
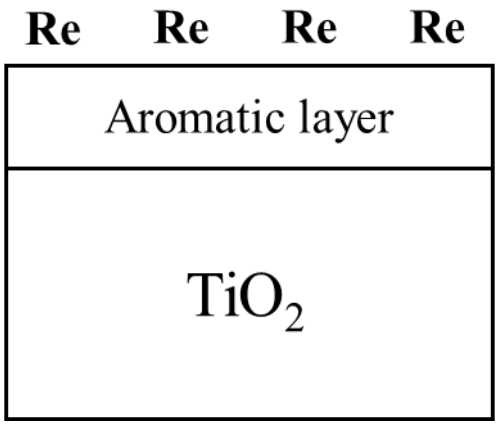


Figure 2. XPS spectra of Re(dcbpy)(CO)$_3$Cl monolayers on TiO$_2$

3.2.3 Data Analysis

Model the XPS of Re-containing monolayers as follows:



Re-containing monolayer: Fraction of monolayers expect $\Phi = 1$

Aromatic layer: This layer scatters Ti photoelectrons but not Re photoelectrons. Model as benzoate layer from Skibinski *et al* (2016)[11]

TiO_2: Semi-infinite TiO_2 slab

Start by calculating the relative density of the Re atoms with regard to bulk Re. Assume the Re is 0.25nm tall. Full monolayer of Re is

$$1 \text{ Re} / 4 \text{ Ti}_{\sigma c}$$

$$= 1 / (13 \text{ Å} \times 5.9 \text{ Å} \times 2.5 \text{ Å})$$

$$= 1 / 0.19 \text{ nm}^3 = 5.3 \text{ nm}^{-3}$$

Number of density of bulk Re = $\left(\frac{21.0\,\text{g}}{cm^3}\right)\left(\frac{1mol}{186.2g}\right)\left(\frac{6.02\times10^{23}}{mol}\right)\left(\frac{cm}{10^7 nm}\right)^3$

$$= 67.9 \text{ nm}^{-3}$$

Monolayer density relative to bulk = 5.3 / 67.9 = 7.8%

Following the derivation in the supporting information for Skibinski *et al* (2016): Integrated area of XPS transition is

$$\frac{\text{I}_{\text{Re}}}{\text{I}_{\text{Ti}}} = \frac{0.078}{0.33}\frac{\Gamma_{Re}}{\Gamma_{Ti}}\frac{\Phi_b}{e^{-\frac{a}{5\lambda_{Ti}cos\theta}}\lambda_{Ti}cos\theta}$$

In this equation, Γ_x represents the XPS cross section of atom X, which is different than the relative sensitivity factor of X, RSF_X. The RSFs are measured on bulk materials and contain contribution from the cross-section and the photoelectron mean free paths (which are energy dependent). The RSFs are tabulated in Wagner, *et al* (1981)[12] Table 3 where RSF≡1. The conversion is

$$\frac{\Gamma_{\text{A}}}{\Gamma_{\text{B}}} = \frac{RSF_A}{RSF_B}\frac{\lambda_B}{\lambda_A}$$

λ_x is photoelectron mean free path of the atom x and the calculation is described in Igor XPS package. Plugging this equation in

$$\frac{\text{I}_{\text{Re}}}{\text{I}_{\text{Ti}}} = 0.24\frac{RSF_{Re}}{RSF_{Ti}}\frac{\lambda_{Ti}}{\lambda_{Re}}\frac{\phi_b}{(0.79)\lambda_{Ti}cos\theta}$$

$$= \ 0.223 \frac{\mathrm{RSF_{Re}}}{\mathrm{RSF_{Ti}}} \frac{1}{\lambda_{Re}} \phi$$

Solving for the frictional density of the Re layer:

$$\phi = 4.48 \frac{\mathrm{RSF_{Ti}}}{\mathrm{RSF_{Re}}} \lambda_{Re} \frac{I_{Re}}{I_{Ti}}$$

Generalize the derivation to any atom X which has a number density of N_X / 4 $Ti_{\sigma c}$ sites

$$\phi = \frac{4.48}{\mathrm{N_x}} \frac{RSF_{Ti}}{RSF_x} \lambda_x \frac{I_x}{I_{Ti}}$$

For the Re monolayer, we expect N_{Re} = 1, N_{Cl} = 1, N_N = 2, N_C = 15

Table 2 shows the absolute monolayer coverage from the C, Re, Cl and N XPS transitions. Complete analysis was performed by Professor **Melissa A. Hines**. If we have a perfect monolayer of the molecule, all entries in the standard variable for surface coverage (Φ) would be 1. However, there is significant number of C than we have expected. The calculation is referenced to the intensity of the Ti $2p_{3/2}$ transition; therefore, the numbers are absolute. The analysis is based on the supplementary information in Erik S. Skibinski, *et al* (2016)[11]. RSF from Table 3 of C.D. Wagner, *et al* (1981)[12]. λ calculated using Hines Lab Igor XPS macros.

Transition	RSF_x	BE (eV)	λ_x (nm)	Γ_x	Integral	N_x	Φ
C 1s	0.25	285.8	1.56	0.160	550850	15	1.83
Ti $2p_{3/2}$	1.2	459.4	1.27	0.945	674634	-	-
O 1s	0.66	-	-	-	1435870	-	-
Re 4f	3.1	42.3	1.86	1.667	214685	1	1.03
Cl 2p	0.73	198.9	1.68	0.435	39992.2	1	0.73
N 1s	0.42	400.6	1.37	0.307	97805.7	2	0.27

Table 2. Full Analysis of XPS data

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CHAPTER 4

RESULTS AND DISCUSSION

Results and Discussion

In order to investigate the molecular orientation of bi-isonicotinic acid, we firstly desired to make a monolayer on TiO_2 surface and performed the experiment to find a good solvent for the molecule. However, discovering a suitable solvent for the molecule was unsuccessful as the solvent candidates behaved poorly in either room temperature condition or in establishing a stable monolayer. These solvents are incompatible with atomic-scale scanning tunneling microscopy (STM) experiments, since many organic solvents leave unwanted residue at the atomic scale.

Re complex was straightforward to synthesize and revealed promising results for future study. Based on the XPS data, we can conclude that there are monolayers of Re complex on the TiO_2 surface. The small amount of extra carbon may be due to adventitious contamination; however, more investigations are needed to determine whether this can be improved by alternative preparation protocols. Overall, calculated values agree well with the absolute values.

CHAPTER 5

CONCLUSION

Conclusion and Future Study

Since the XPS data of Re complex show promising results, we suggest scanning tunneling microscopy (STM) investigations of $Re(dcbpy)(CO)_3Cl$ adsorption on TiO_2 in order to acquire topological information. Getting regional information of molecular pairing or spacing will provide insight on the configuration of the ligand molecules.

If the STM investigation of Re complex is accomplished successfully, we can then understand the behavior of bi-isonicotinic acid of the complex better and restart the first experiment under different conditions.

Our final goal is to characterize bi-isonicotinic acid on atomically flat TiO_2 surface and thoroughly understand how the molecule is electronically conjugated to surface. Moreover, discovering orientation of the molecule can be extended into finding methods of attaching molecules onto surface. Managing molecules can give an opportunity to build-up metals or bigger structures such as Metal-Organic Frameworks (MOFs), which may introduce a new class of photovoltaic cell.

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